



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p style="text-align: center;">SEARCHED 01 MAR 2000</p> <p>Title: PACKAGING MATERIAL</p> <p>Abstract</p> <p>A flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38 °C and 90 % relative humidity is disclosed. It contains (a) a layer of paper having a weight between 20 and 400 g/m², (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b). This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine.</p>			

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TITLE

PACKAGING MATERIAL

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The present invention relates to packaging for food products that are sensitive to oxidation, including dairy products such as cheese, butter and margarine.

Background of the invention

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Various materials for providing oxygen barriers for products sensitive to oxidation are known, including ethylene vinyl alcohol (EVOH), amorphous nylon, semicrystalline polyamide 6 and polyacrylonitrile.

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For packaging liquid or semi-liquid materials that are sensitive to oxidation, water barrier properties are also needed. C.f. EP 0241 819, which discloses a laminate using nylon as a barrier; EP 0293 098, which discloses a multilayer structure with EVOH and low density polyethylene (LDPE) coated on board. More recently, EP 0520 767 discloses the use of amorphous nylon as a non-foil composite laminate. In all of these cases, water vapor transmission is below 10 g/m²d due to a relatively thick polyethylene seal layer.

20

In soft cheese packaging the right balance of an oxygen barrier and a moisture barrier is given by a cellulosic film laminate to paper. In this case, the water vapor transmission is between 400 and 630 g/m²d at 38 °C and 90% relative humidity (RH), while the oxygen permeability is below 10 cc/m²d atm.

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Summary of the invention

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The present invention provides a flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38°C and 90% relative humidity comprising (a) a layer of paper having a weight between 20 and 400 g/m², (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b). This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine.

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The packaging material may be made by means known in the art such as by coextrusion coating or lamination of coextruded film onto paper.

Detailed description of the invention

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As used herein, the following terms have the meanings given below.

'Flexible packaging material' means packaging sheet material suitable for wrapping goods, e.g. the aforementioned dairy products. 'Semi-flexible packaging material'

means packaging material having a somewhat higher resistance to flex, typically having a board (e.g. cardboard) as paper layer (a). Semi-flexible packaging material may be thermoformed, as known in the art, to form desired shapes, such as trays.

5 ‘Oxygen barrier’ measures the rate at which oxygen passes through the packaging material of the present invention, and is between 10 and 100 cc/m²d atm measured according to ASTM D 3985.

10 ‘Water vapor barrier’ measures the rate at which water vapor passes through the packaging material of the present invention, and is between 100 and 1000 g/m²d at 38°C and 90% relative humidity.

15 Paper layer (a) can be any type of paper typically used in the packaging industry, flexible or semi-flexible, and having a weight between 20 and 400 g/m². This weight governs the degree of flexibility of the paper. Paper, being a very porous material, does not control the oxygen or water vapor barrier properties of the packaging material of the present invention.

20 The ethylene copolymer of layer (b) can be ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or ethylene butyl acrylate, an ethylene-acid copolymer or its corresponding ionomer.

25 The ethylene-acid copolymers are copolymers of ethylene and α,β-ethylenically-unsaturated C₃-C₈ carboxylic acid have the acid moiety present in an amount of 1 to about 25, (preferably 6 to 9) wt. % of the copolymer. The preferred acid moieties are methacrylic acid and acrylic acid.

30 The ethylene-acid copolymers can also be E/X/Y copolymers where E is ethylene; X is a softening comonomer and Y is the α,β-ethylenically-unsaturated C₃-C₈ carboxylic acid, particularly acrylic or methacrylic acid. By “softening”, it is meant that the polymer is made less crystalline. Suitable “softening” comonomers (X) are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1 - 12 carbon atoms which, when present, may be up to 25 (preferably up to 15, most preferably up to 10) wt. % of the ethylene-acid copolymer.

35 Specific ethylene-acid copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate.

40 Corresponding ionomers of the ethylene-acid copolymers are formed by partially neutralizing the acid moiety. The acid moiety is partially neutralized with monovalent and/or bivalent metal cations such as lithium, sodium*, potassium, magnesium, calcium, barium, lead, tin, zinc* or aluminum (*= preferred), or a combination of such

cations. The mole percent of acid neutralized is up to about 70 %, preferably 30 to 50 %.

5 Ionomers can be made by processes well known in the art (cf. U.S. Pat. No. 3,262,272 to Rees, for example).

The graft of the ethylene copolymer will be maleic anhydride, typically in an amount between 0.1 and 3 weight %. Grafting can be carried out using techniques known in the art.

10 Optionally, layer (b) may further comprise up to 40 weight % of a copolyether ester, a copolyether amide or a polyurethane thermoplastic. Suitable copolyether esters are available under the name Hytrel® from the DuPont Company; suitable copolyether amides are available under the name Pebax® from Elf Atochem.

15 Layer (b) will be applied to paper layer (a) at a weight between 1 and 5 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met. Suitable ethylene copolymers for use in layer (b) are the Bynel® and Surlyn® families of resins, both available from the DuPont Company.

20 Nylon layer (c) can contain pure amorphous nylon or can be a blend of between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6.

25 The term "amorphous polyamide" is well known to those skilled in the art. "Amorphous polyamide", as used herein, refers to those polyamides which are lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter ("DSC") measurement (ASTM D-3417), 10 °C/minute.

30 Examples of the amorphous polyamides that can be used include those amorphous polymers prepared from the following diamines: Hexamethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, bis-(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidine, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, meta-xylylenediamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethylaminobutane, 1,4-diaminomethylcyclohexane, p-xylylenediamine, m-phenylenediamine, p-phenylenediamine, and alkyl substituted m-phenylenediamine and p-phenylenediamine.

35 40 Examples of polyamides that can be used include those amorphous polymers prepared from the following diacarboxylic acids: isophthalic acid, terephthalic acid, alkyl substituted iso- and terephthalic acid, adipic acid, sebacic acid, butane dicarboxylic acid, and the like.

45 Specific examples of amorphous polyamides which are suitable for this invention include: hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide, copolymers of hexamethylene diamine and 2-

methylpentamethylenediamine with iso-or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful provided a second diamine such as 2-methyldiaminopentane is incorporated to produce a processible amorphous polymer.

The above amorphous polyamides may contain as comonomers minor amounts of lactam species such as caprolactam or lauryl lactam, even though polymers based on these monomers alone are not amorphous. The important feature is that the polyamide as a whole must be amorphous. Thus small amounts of these comonomers may be incorporated as long as they do not impart crystallinity to the polyamide. In addition, up to about 10 weight % of a liquid or solid plasticizer such as glycerol, sorbital, mannitol, or aromatic sulfonamide compounds (such as Santicizer 8® from Monsanto) may be included with the amorphous polyamide.

A suitable amorphous polyamide for use in the present invention is available from the DuPont Company under the tradename SELAR®PA.

The term "semicrystalline polyamide 6" is well known to those skilled in the art. Semicrystalline polyamide 6 suitable for this invention are generally prepared from lactams or amino acids or from condensation of diamines such as hexamethylene diamine with dibasic acids such as sebacic acid. Copolymers and terpolymers of these polyamides are also included. A suitable semicrystalline polyamide 6 for use in the present invention is Durethan® B29, available from Bayer.

Layer (c) will be applied to paper layer (b) at a weight between 10 and 30 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met.

This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine. It will be typically be produced by coextrusion coating of layers (b) and (c) onto layer (a), or by lamination of extruded or coextruded layers (b) and (c) onto layer (a). Optionally, the so prepared packaging material can be subsequently thermoformed into a desired shape, such as a tray.

Example 1

Layer (b) of ByneL® 21E533 (an anhydride modified ethylene acrylate resin from DuPont) is coextruded with layer (c) of various blend of Selar® PA 3426 (an amorphous nylon from DuPont) and Durethan® B29 (a semicrystalline polyamide 6 from Bayer) and coated on paper.

The nylon blend is introduced into a 3.5" extruder with barrel temperatures set at 240, 280, 280, 280 and 280 °C. The ByneL® 21E533 is introduced in 2.5" extruder with barrel temperatures set at 180, 220, 250, 270, 280 °C. Feed bloc and die temperatures are set at 280°C.

The 800 mm wide die is 150 mm (air gap) above the nip where it coats the paper. The paper is corona treated and run at the line speed of 200 m/min. The final so produced structure is:

5 paper // The Bynel® 21E533 // Selar® PA3426+Durethan® B29
 40 g/m² 2 g/m² 12 g/m²

The following water transmission (38°C, 90% RH) and oxygen permeability (room temperature) is measured (% given by weight):

	Example		water g/ m ² d	oxygen cc/ m ² d atm
15	1.1 80% Selar® PA3426 + 20% Durethan® B29		400	32
	1.2 50% " + 50% "		500	35
	1.3 20% " + 80% "		800	43

The last two structures are particularly well suited for soft cheese packaging.

20 Example 2

Example 1 is repeated except that Surlyn® AD2 is substituted for Bynel® 21E533.

25 Surlyn® AD2 (2 g/m²) is coextruded with the blend 80 weight % Selar® PA3426 + 20 weight % Durethan® B29 (12 g/m²). The oxygen permeability is the same as in Example 1.1. Water permeability lowers to 250 g/m²d.

This structure when extruded on a glossy chill-roll has a very glossy appearance. Together with the dead-foil, it can be used for candy and butter wrapping.

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Example 3

35 Example 2 is repeated except that the paper layer is replaced with board having a weight of 200 g/m². The board can be thermoformed to produce trays or lidding.

Example 4

40 Example 1 is repeated except that the 70 wt. % Bynel® 21E533 and 30 wt % Hytrel® 3548 is substituted for Bynel® 21E533.

Claims

1. A flexible or semi-flexible packaging material with an oxygen barrier between 5 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38°C and 90% relative humidity comprising
 - (a) a layer of paper having a weight between 20 and 400 g/m²
 - (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and
 - (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b).
2. The packaging material of claim 1 wherein the ethylene copolymer of layer (b) is ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or ethylene butyl acrylate.
3. The packaging material of claim 1 wherein the ethylene copolymer of layer (b) is an ethylene-acid copolymer or its corresponding ionomer.
4. The packaging material of claim 1 wherein the grafted ethylene copolymer of layer (b) is a maleic anhydride grafted ethylene copolymer.
5. The packaging material of any one of claims 1 to 4 wherein layer (b) further comprises up to 40 weight % of a copolyether ester, a copolyether amide or a polyurethane thermoplastic.
6. The packaging material of any one of claims 1 to 5 which is produced by coextrusion coating layers (b) and (c) onto layer (a).
7. The packaging material of any one of claims 1 to 5 which is produced by lamination of extruded or coextruded layers (b) and (c) onto layer (a).

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/34 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 551 366 A (MARUHASHI YOSHITSUGU ET AL) 5 November 1985 see column 2, line 26-41 - column 4, line 49-65-66; claims 1,3,4,7,8,17; figures 1,3,4,7,8	1,4,6
Y	see column 5, line 3-19-25 - column 7, line 65-68 see column 8, line 5-19-25 - line 39-43 see column 9, line 64-67 - column 10, line 4-20-57	1-3
Y	DE 40 26 040 A (PKL VERPACKUNGSSYSTEME GMBH) 8 August 1991 see column 1, line 49; claims 1,2	1-4,6,7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

17 December 1998

Date of mailing of the international search report

30/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Derz, T

INTERNATIONAL SEARCH REPORT

Report No. Application No.

PCT/US 98/18731

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 687 557 A (ENSO GUTZEIT OY) 20 December 1995 see column 3, line 12-43; claims 4,9,10; figures 3,4 ----	1,4,6,7
A	EP 0 520 767 A (WESTVACO CORP) 30 December 1992 cited in the application see claims 1,4,5; figure 3A ----	1,4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Application No.
PCT/US 98/18731

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4551366 A	05-11-1985	JP 1384118 C JP 58154755 A JP 61049341 B AU 557675 B AU 1001583 A EP 0084421 A ZA 8300079 A		09-06-1987 14-09-1983 29-10-1986 08-01-1987 18-08-1983 27-07-1983 29-02-1984
DE 4026040 A	08-08-1991	EP 0441234 A		14-08-1991
EP 0687557 A	20-12-1995	FI 942877 A AU 695041 B AU 2171395 A JP 8002555 A US 5840385 A		17-12-1995 06-08-1998 04-01-1996 09-01-1996 24-11-1998
EP 0520767 A	30-12-1992	CA 2070349 A JP 2537000 B JP 5229070 A MX 9202891 A		27-12-1992 25-09-1996 07-09-1993 01-12-1992

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

Date of mailing (day/month/year)
20 May 1999 (20.05.99)

To:
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in its capacity as elected Office

International application No.
PCT/US98/18731

Applicant's or agent's file reference
AD6530

International filing date (day/month/year)
08 September 1998 (08.09.98)

Priority date (day/month/year)
08 September 1997 (08.09.97)

Applicant

TROUILHET, Yves

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

29 March 1999 (29.03.99)

in a notice effecting later election filed with the International Bureau on:

2. The election was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

F. Baechler

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
E.I. DU PONT DE NEMOURS AND COMPANY
 Legal/Patent Records Center
 Attn. EVANS, C.
 1007 Market Street
 Wilmington, Delaware 19898
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JAN 20, 1999

Date of mailing (day/month/year)	30/12/1998
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Applicant's or agent's file reference
AD6530

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/US 98/ 18731

International filing date
(day/month/year)
08/09/1998

Applicant

E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
 34, chemin des Colombettes
 1211 Geneva 20, Switzerland
 Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority
 European Patent Office, P.B. 5818 Patentlaan 2
 NL-2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Cristina Iacoponi

CLS NOTED

1,13,99

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the International application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]: "Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]: "Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]: "Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or "Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]: "Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference AD6530	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 98/18731	International filing date (day/month/year) 08/09/1998	(Earliest) Priority Date (day/month/year) 08/09/1997
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of **3** sheets.

It is also accompanied by a copy of each priorart document cited in this report.

1. Certain claims were found unsearchable (see Box I).
2. Unity of invention is lacking (see Box II).
3. The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
 - filed with the international application.
 - furnished by the applicant separately from the international application,
 - but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
 - Transcribed by this Authority
4. With regard to the title, the text is approved as submitted by the applicant
 the text has been established by this Authority to read as follows:
5. With regard to the abstract,
 - the text is approved as submitted by the applicant
 - the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.
6. The figure of the drawings to be published with the abstract is:
Figure No.
 - as suggested by the applicant.
 - because the applicant failed to suggest a figure.
 - because this figure better characterizes the invention.

None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/18731

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B32B27/34 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
 IPC 6 B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 551 366 A (MARUHASHI YOSHITSUGU ET AL) 5 November 1985 see column 2, line 26-41 - column 4, line 49-65-66; claims 1,3,4,7,8,17; figures 1,3,4,7,8	1,4,6
Y	see column 5, line 3-19-25 - column 7, line 65-68 see column 8, line 5-19-25 - line 39-43 see column 9, line 64-67 - column 10, line 4-20-57 ---	1-3
Y	DE 40 26 040 A (PKL VERPACKUNGSSYSTEME GMBH) 8 August 1991 see column 1, line 49; claims 1,2 ---	1-4,6,7 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

17 December 1998

30/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Derz, T

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 98/18731

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 687 557 A (ENSO GUTZEIT OY) 20 December 1995 see column 3, line 12-43; claims 4,9,10; figures 3,4 ---	1,4,6,7
A	EP 0 520 767 A (WESTVACO CORP) 30 December 1992 cited in the application see claims 1,4,5; figure 3A -----	1,4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/US 98/18731

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4551366	A 05-11-1985	JP 1384118 C JP 58154755 A JP 61049341 B AU 557675 B AU 1001583 A EP 0084421 A ZA 8300079 A		09-06-1987 14-09-1983 29-10-1986 08-01-1987 18-08-1983 27-07-1983 29-02-1984
DE 4026040	A 08-08-1991	EP 0441234 A		14-08-1991
EP 0687557	A 20-12-1995	FI 942877 A AU 695041 B AU 2171395 A JP 8002555 A US 5840385 A		17-12-1995 06-08-1998 04-01-1996 09-01-1996 24-11-1998
EP 0520767	A 30-12-1992	CA 2070349 A JP 2537000 B JP 5229070 A MX 9202891 A		27-12-1992 25-09-1996 07-09-1993 01-12-1992

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E.I. DU PONT DE NEMOURS AND COMPANY
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9 ^{NOTIFICATION}
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

01.07.99

Applicant's or agent's file reference
AD6530

IMPORTANT NOTIFICATION

International application No.
PCT/US98/18731International filing date (day/month/year)
08/09/1998Priority date (day/month/year)
08/09/1997

Applicant

E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

7.8.99

TRB NOTED

Name and mailing address of the IPEA/

Authorized officer

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Ridé, M-C

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AD6530	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US98/18731	International filing date (day/month/year) 08/09/1998	Priority date (day/month/year) 08/09/1997
International Patent Classification (IPC) or national classification and IPC B32B27/34		
<p>Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.</p>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 		

Date of submission of the demand 29/03/1999	Date of completion of this report 01.07.99
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Giese, H-H Telephone No. (+49-89) 2399



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/18731

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-5 as originally filed

Claims, No.:

1-7 as originally filed

2. The amendments have resulted in the cancellation of:

the description, pages:
 the claims, Nos.:
 the drawings, sheets:

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-7
	No: Claims
Inventive step (IS)	Yes: Claims 1-7
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-7
	No: Claims

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/18731

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/18731

1. Prior art does not teach the subject-matter of claims 1 to 7. Thus they are regarded to be novel and to meet the requirements of Article 33(2) PCT.
2. The technical problem to be solved by the present invention was to provide a flexible/semi-flexible packaging material which has specific oxygen and water vapour permeabilities.

In the application the problem was solved by means of a three-layer composite comprising first a layer of paper (a), second a layer of ethylene copolymer or grafted ethylene copolymer (b) and finally a layer of nylon (c) comprising amorphous nylon and optionally semicrystalline polyamide 6.

- 2.1. Closest prior art document US-A-4 551 366 relates to a flexible layered composite vessel for food preservation which can be easily opened, retrains its shape even when the internal pressure drops and exhibits low permeabilities to oxygen and water vapours. The pre-formed packaging material comprises a cup-shaped outer paper membrane (50-400 g/m²) and a flexible seamless cup-shaped inner member composed of a gas-barrier plastic material. The inner member was molded through a T-die into a sheet and is exactly fitted into the outer membrane. The inner member is preferably made of a laminated or coated film comprising a blend of ethylene-vinyl alcohol copolymer and a copolyamide.
- 2.2. Neither US-A-4 551 366 nor any of the other documents from the international search report suggests that a layer consisting solely of nylon in combination with the other features of present claim 1 would lead to the oxygen and water vapour permeabilities sought by the present application.
- 2.3. Independent claims 1, 6 and 7 as well as dependent claims 2 to 5 therefore also exhibit an inventive step (Article 33(3) PCT).

DR
PATENT COOPERATION TREATY**PCT**

REC'D 05 JUL 1999	
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AD6530	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US98/18731	International filing date (day/month/year) 08/09/1998	Priority date (day/month/year) 08/09/1997
International Patent Classification (IPC) or national classification and IPC B32B27/34		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application</p>		

Date of submission of the demand 29/03/1999	Date of completion of this report 01.07.99
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Giese, H-H Telephone No. (+49-89) 2399



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/18731

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

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Claims, No.:

1-7 as originally filed

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the description, pages:
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 the drawings, sheets:

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-7
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-7
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-7
	No:	Claims	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/18731

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/18731

1. Prior art does not teach the subject-matter of claims 1 to 7. Thus they are regarded to be novel and to meet the requirements of Article 33(2) PCT.
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In the application the problem was solved by means of a three-layer composite comprising first a layer of paper (a), second a layer of ethylene copolymer or grafted ethylene copolymer (b) and finally a layer of nylon (c) comprising amorphous nylon and optionally semicrystalline polyamide 6.

- 2.1. Closest prior art document US-A-4 551 366 relates to a flexible layered composite vessel for food preservation which can be easily opened, retrains its shape even when the internal pressure drops and exhibits low permeabilities to oxygen and water vapours. The pre-formed packaging material comprises a cup-shaped outer paper membrane (50-400 g/m²) and a flexible seamless cup-shaped inner member composed of a gas-barrier plastic material. The inner member was molded through a T-die into a sheet and is exactly fitted into the outer membrane. The inner member is preferably made of a laminated or coated film comprising a blend of ethylene-vinyl alcohol copolymer and a copolyamide.
- 2.2. Neither US-A-4 551 366 nor any of the other documents from the international search report suggests that a layer consisting solely of nylon in combination with the other features of present claim 1 would lead to the oxygen and water vapour permeabilities sought by the present application.
- 2.3. Independent claims 1, 6 and 7 as well as dependent claims 2 to 5 therefore also exhibit an inventive step (Article 33(3) PCT).

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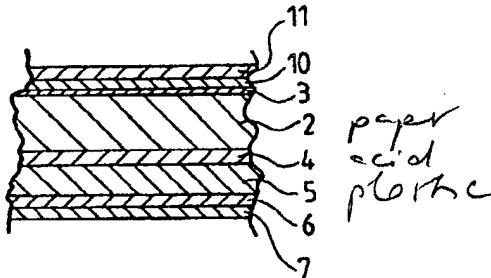
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 27/10, B65D 65/40	A1	(11) International Publication Number: WO 95/10413 (43) International Publication Date: 20 April 1995 (20.04.95)
(21) International Application Number: PCT/FI94/00453		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).
(22) International Filing Date: 10 October 1994 (10.10.94)		
(30) Priority Data: 934476 11 October 1993 (11.10.93) FI		
(71) Applicant (<i>for all designated States except US</i>): YHTYNEET PAPERITEHTAAT OY [FI/FI]; FIN-37600 Valkeakoski (FI).		Published <i>With international search report.</i>
(72) Inventors; and		
(75) Inventors/Applicants (<i>for US only</i>): HÄKKINEN, Leena [FI/FI]; Kaaponkuja 3, FIN-33820 Tampere (FI). KARHUKETO, Hannu [FI/FI]; Asevelitie 11, FIN-37630 Valkeakoski (FI). OLLILA, Hannu [FI/FI]; Leikkaantie 9, FIN-37680 Valkeakoski (FI).		
(74) Agent: OY KOLSTER AB; Iso Roobertinkatu 23, P.O. Box 148, FIN-00121 Helsinki (FI).		

(54) Title: LID FOR A FOOD CAN



(57) Abstract

A lid for a food can, comprising a body layer (2) made of paper, a plastic layer composite (4, 5, 6) extruded onto that surface of the body layer that faces the can and, attached to the plastic layer composite, a peelable heat-sealing layer (7) for fastening the lid (1) to the can by heat-sealing. According to the invention, the heat-sealing layer comprises a layer (7) of heat-sealing lacquer, and the plastic layer composite comprises, adjacent to the paper layer (2), a first plastic layer (4) made of acid-modified ethylene-based copolymer, adjacent to the first plastic layer, a second plastic layer (5) made of plastic that is infusible at the heat-sealing temperature used; and between the second plastic layer (5) and the heat-sealing lacquer (7), a third plastic layer (6) made of acid-modified ethylene-based copolymer.

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Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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GA	Gabon				

Lid for a food can**Background of the invention**

5 The invention relates to a lid for a food can, comprising a body layer made of paper, a plastic layer composite extruded onto that surface of the body layer that faces the can and, attached to the plastic layer composite, a peelable heat-sealing layer for fastening the lid to the can by heat-sealing.

10 The term 'to peel' is used herein to mean the opening of a relatively fast joint in a predetermined manner without that it tears.

15 A lid for a food can as described above is known e.g. from Finnish Patent Application 914,268. In the lid for a food can described in the application, aluminium, which is conventionally used in cans for yoghurt, pudding, and other corresponding products, has been replaced with a paper-based material. The surface of the lid that faces the can is coated with a plastic layer composite by extruding in one step, the most essential layers of the composite being an oxygen-impermeable layer and a heat-sealable polymer layer facing the can. Further, on both sides of the oxygen-permeable layer are extruded polymeric adhesive layers.

20 Production of a lid for a food can as described above includes several contributing factors that must have a defined relationship to one another in order that the product might function as desired. A particular problem in the production of paper-based lids for food cans is the tendency of the lids to curl. The primary reason for this is that the plastic layers have a different crystallization degree and coefficient of heat expansion. In fact, various kinds of trial runs must be conducted to obtain a composition in which the forces that make the product curl are in balance such that the

lid keeps straight. Further, the lid must comprise plastic layers that are able to adjust themselves to any unevenness on the jointing surface of the can, so that the joint is uniform and tight. Another major problem involved in joint sealing is that it must be possible to detach the lid from the can in one piece without using excessive force. On account of this, it must be possible to control the heat-sealing temperature very accurately, so that a desired result can be achieved.

5 In addition, adhesion between the different layers of an extruded plastic composite must be so great that the lid does not peel from between these layers but that it can be detached from the can in one piece.

10

A problem with the lid according to the above-mentioned Finnish Patent Application 914,268 is that the temperature range at which heat-sealing can be successfully conducted is narrow. Although with modern packing machines the heat-sealing temperature can be adjusted very accurately, practice has shown that to make it possible to perform heat-sealing reliably and successfully in all conventional packing machines, heat-sealing temperature variation must be dozens of degrees.

15

Further, it is advantageous if the lid is also suitable for frozen products, such as ice lolly packs, replacing the aluminium lid conventionally used in them also. The glass transition temperature of the plastic layers used must be sufficiently low so that the pack functions reliably in freezing temperatures also.

20

30 Summary of the Invention

The above objectives can be reached and problems solved by the food can lid described in the present application, the lid being characterized in that the heat-sealing layer comprises a layer of heat-sealing lacquer, and that the plastic layer composite comprises,

35

5 adjacent to the paper layer, a first plastic layer made of acid-modified ethylene-based copolymer; adjacent to the first plastic layer, a second plastic layer made of plastic that is infusible at the heat-sealing temperature used; and between the second plastic layer and the heat-sealing lacquer, a third plastic layer made of acid-modified ethylene-based copolymer.

10 The second plastic layer advantageously comprises a polyamide layer. Alternatively, the second plastic layer comprises a layer of polyolefin-based plastic. The polyolefin-based plastic is typically, for example, polyethylene, polypropylene or polybutylene.

15 Typically, the acid-modified ethylene-based copolymer may be e.g. ethylmethylacrylate, ethylbutyl-acrylate, ethylvinylacetate, ethylacrylic acid or ethyl-methylacrylic acid. The copolymer may also be any one of the above-listed copolymers further modified with maleic acid.

20 Brief Description of the Drawings

In the following, the lid for a food can according to the invention and especially the material composition thereof are described in greater detail with reference to the attached drawing, wherein

25 Fig. 1 shows a top view of an exemplary embodiment of a lid according to the invention, and

Fig. 2 shows a cross-sectional view of the lid shown in Fig. 1.

30 Description of the Preferred Embodiment

Fig. 1 shows an exemplary embodiment 1 of the lid for a food can according to the invention, comprising a generally circular body element 8 and a tab 9 connected therewith. The lid is intended to be heat-sealed, close to the outer edge of its circular

body element 8, onto a flange formed at the upper edge of a circular can.

Fig. 2 shows a cross-section of the lid 1 shown in Fig. 1. The lid comprises a body layer 2 made of paper, coated with a mineral coating 3. On top of the mineral coating 3 is a printing layer 10, and on top of that is protective lacquer 11. When mineral-coated paper is used, the print results are excellent. The protective lacquer, on the other hand, makes the print sufficiently moisture-resistant and sufficiently protects the paper layer 2 from external moisture.

On the lower surface of the paper layer 2, i.e. on the surface that faces the can, there is first a plastic layer 4 that is made of acid-modified ethylene-based copolymer (hereinafter: EAM) and that adheres well to paper, sealing the surface that faces the can. The EAM layer primarily functions as an adhesive layer, making it possible for the different parts of the plastic layer composite to attach to one another. Onto the lower surface of the EAM layer 4 is extruded, simultaneously with layer 4, a polyamide layer 5, which gives the lid the properties desired, particularly as regards gas permeability. Layer 5 could not be attached directly to the paper layer 2, since its adheres to paper rather poorly. Simultaneously, onto the lower surface of the plastic layer is also extruded a third plastic layer 6, which is also made of acid-modified ethylene-based copolymer (EAM). This EAM layer 6 also functions as an intermediate layer between layer 5 and a heat-sealing lacquer layer 7 applied to its lower surface. In addition, EAM layer 6 prevents moisture from entering layer 5. If moisture had an access to the polyamide layer, the layer would swell, damaging the lid. The characteristics of the heat-sealing lacquer 7, on the other hand, are such that the lacquer would not adhere directly to the

polyamide layer 5 to the extent desired. Layer 6 is thus, in practice, essential.

Layers 4 and 6 help to render the part of the lid comprising layers 2, 4, 5, 6 and 7 such that it does not tend to curl, nor do the layers detach from one another, not even under moist conditions. Layer 7 makes it possible to heat-seal the lid to the body of the can. The melting point of layer 5 must be such that the layer hardly melts at all at the heat-sealing temperature. On the other hand, layers 4 and 6 soften during heat-sealing to such an extent that they are able to level down any unevenness present on the adhesion surface of the can: e.g. layer 4 may penetrate to some extent between the fibres of the paper layer 2.

The lid according to the invention also resists freezing, since the glass transition temperature of EAM is sufficiently low. The lid is thus also suited for cans used in packing ice-cream or ice lollies or other corresponding frozen products.

The effectiveness of the lid according to the invention is especially based on the advantageous properties of the EAM layers 4 and 6. This material adheres to both paper, polyamide and heat-sealing lacquer to a sufficient degree, and it is sufficiently watertight to protect the polyamide layer 5 against moisture. Further, it softens at the heat-sealing temperature used and is thus able to function as a levelling layer in the above manner. The essential feature of the lid according to the invention is that the properties (e.g. crystallization of plastics and coefficients of heat-expansion) of the mineral-coated paper and the multi-layer film comprising three plastic layers extruded thereon are in balance, whereby the product keeps straight. This is essential, since otherwise the material would not be suitable for use as a lid for a food can, attachable by

heat-sealing. In addition, when heat-sealing lacquer 7 instead of e.g. an EAM plastic layer is used in heat-sealing, the heat-sealing temperature may very dozens of degrees, since the peeling range of the heat-sealing lacquer is about 50°C. Further, the heat-sealing lacquer 7 encloses EAM layer 6, thereby improving the useability of the lid for a food can.

A lid for a food can has been described above by means of one exemplary embodiment, and it is to be understood that it can be modified in many ways without deviating from the scope defined by the attached claims. The polyamide layer can thus be replaced by plastic, especially propene-based plastic, having the desired properties, such as infusibility at the heat-sealing temperature used. Likewise, the surface layers 10 and 11 can be modified as desired. It is noted, however, that protection of a mineral-coated paper against external moisture by means of protective lacquer rather than a plastic layer also renders the material used in the present lid pulpable, which is clearly advantageous.

Claims

1. A lid for a food can, comprising a body layer (2) made of paper, a plastic layer composite (4, 5, 6) extruded onto that surface of the body layer that faces the can and, attached to the plastic layer composite, a peelable heat-sealing layer (7) for fastening the lid (1) to the can by heat-sealing, characterized in that the heat-sealing layer comprises a layer (7) of heat-sealing lacquer, and that the plastic layer composite comprises, adjacent to the paper layer (2), a first plastic layer (4) made of acid-modified ethylene-based copolymer; adjacent to the first plastic layer, a second plastic layer (5) made of plastic that is infusible at the heat-sealing temperature used; and between the second plastic layer (5) and the heat-sealing lacquer (7), a third plastic layer (6) made of acid-modified ethylene-based copolymer.

2. The lid for a food can according to claim 1, characterized in that the second plastic layer comprises a polyamide layer (5).

3. The lid for a food can according to claim 1, characterized in that the second plastic layer comprises a layer (5) of polyolefin-based plastic.

1/1

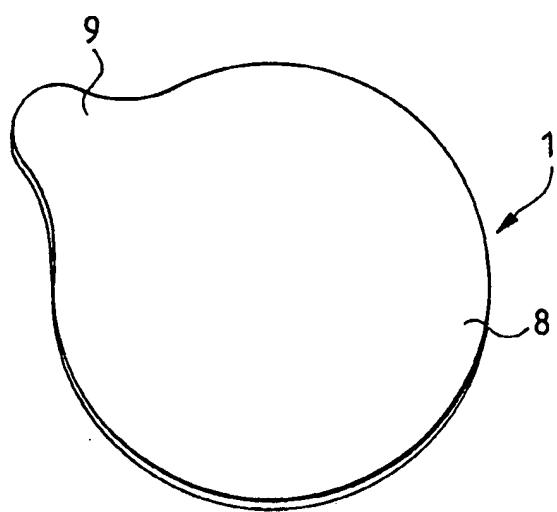


FIG. 1

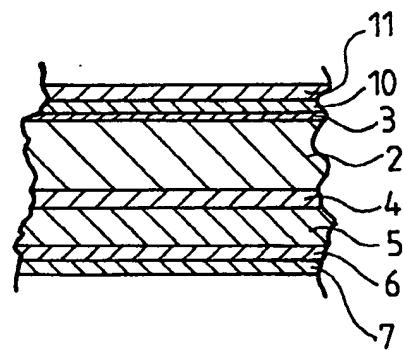


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00453

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 27/10, B65D 65/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B32B, B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A1, 9204187 (ENSO-GUTZEIT OY), 19 March 1992 (19.03.92), page 5, line 17 - page 6, line 4, claims 1, 4, 7 and 8 --	1-3
A	EP, A1, 0520767 (WESTVACO CORPORATION), 30 December 1992 (30.12.92), page 4, line 27 - line 31, line 44 - line 53, fig. 3a -----	1-3

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 9204187	19/03/92	AU-A-	8419591	30/03/92
EP-A1- 0520767	30/12/92	CA-A- JP-A-	2070349 5229070	27/12/92 07/09/93

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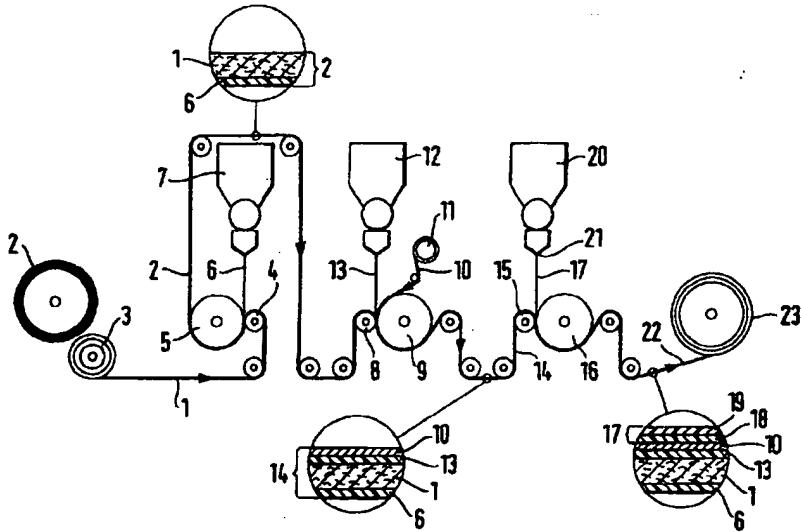
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(54) Title: A METHOD OF AND APPARATUS FOR USE IN MANUFACTURING A PACKAGING LAMINATE



(57) Abstract

In an extrusion laminating system for production of a laminate for packaging liquid food, a thermoplastics product-contact layer (19) is extrusion coated onto an oxygen barrier substrate (10) from a low-temperature extruder (20), without the thermoplastics reaching its breakpoint temperature prior to its entry into the extruder (20) or at any point between its entry into the extruder (20) and arrival at a chill roller (16) immediately downstream of a die slot (21) of the extruder (20). Thereby, transmittal of off-flavour-producing compounds from the laminate to the liquid food can be avoided. Adhesion between the product-contact layer (19) and the substrate (10) is promoted in one or more of a number of ways, for example by co-extrusion of the product-contact layer (19) with a tie layer (18), to provide good adherence of the product-contact layer (19) in spite of its low-temperature extrusion.

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**A METHOD OF AND APPARATUS FOR USE IN MANUFACTURING A
PACKAGING LAMINATE**

This invention relates to a method of and apparatus for use in manufacturing a packaging laminate.

5 The desire of US-A-4,657,614 is to build up a packaging laminate which has a carrier layer of paper, cardboard or for example polystyrene foam, whereby packages manufactured from the laminate can be formed by folding to a lasting shape and a good mechanical protection is imparted to the contents.

10 Moreover, the desired laminate should be liquid-tight so as not to absorb moisture or liquid which may come into contact with the outside of the package, and the package should have an inside which is liquid-tight and which can be heat-sealed by bringing together plastics layers which can be fused

15 together with the help of heat and pressure to a mechanically strong union. Furthermore, the inner plastics layer, which is in direct contact with the contents, should have a low characteristic taste level in cases where the contents are constituted of foodstuffs. The inner plastics layer should

20 desirably be sufficiently strong and tough to withstand the stresses on the material occasioned by the fold-forming without causing the plastics to split. Furthermore, the desired laminate should include a gas barrier layer, preferably of aluminium (Al) foil. Thus, a number of different

25 material layers are joined to one another and this is done with the help of different binder layers.

US-A-4,657,614 adds that, conventionally, when manufacturing such a packaging laminate, broadly speaking, two differing methods are used. The first method is a dry laminating method, in which, after applying adhesive to laminated material (sub-substrate) such as a film made from plastics and drying the same, such a sub-substrate is pasted to the surface of the substrate. The second method is an extrusion laminating method, in which a thin layer of plastics melted at a temperature as high as 300°C, is extruded from an extrusion die and coating of the plastics is formed on the surface of the Al foil. Packaging comprised of such laminate manufactured by either conventional method can

have an off-flavour which may be transferred to the contents. Such an improper change is more frequently found whenever the contents are packaged for longer preservation or at higher temperature. That is because, for packaging laminate
5 manufactured by the dry laminating method, for example, there exists a layer of adhesive between the Al foil and the plastics layer located at the inner surface of the packaging container and the adhesive is eluted. On the other hand, the extrusion laminating method causes oxidative product
10 (carboxyl group) in the plastics, and the oxidative product gives an abnormal smell and deterioration of the flavour.

US-A-4,657,614 further discloses that a packaging container to be filled with a drink is not only required to have sufficient strength that the container may not be deformed, but also it is necessary that the inner plastics layer be firmly adhered to the Al foil so that leakage of the drink be prevented. The Patent states that, to adhere the plastics firmly to the Al foil, in the case of polyethylene (PE), for example, the PE needs to be extruded at a high
15 temperature over 300°C. The plastics which is extruded at the high temperature sticks well to the surface of the aluminium foil, but, owing to its contact with the air for a relatively long time before forming a thin layer on the foil, produces a high proportion of oxidative product. Conversely, if the
20 plastics is maintained at a lower temperature so as to prevent the formation of the oxidative product, the adherence with the foil becomes weaker and the workability of the container becomes worse. The oxidative product existing in the layer of plastics is gradually eluted into the packaged
25 contents particularly in the situation of higher temperatures, wherein the degree of elution is increased.
30

US-A-4,657,614 concluded that, for those reasons, a package using the laminate manufactured by a conventional method could not be readily heated so as to preserve food sensitive to taste and flavour for a long time.
35

The solution proposed by US-A-4657614 to those conventional difficulties was to extrude a film of melted plastics between a substrate web and an Al foil web while a

web of blown synthetic resin film was positioned at the opposite side of the Al foil, and then to pass these materials between a pair of rollers, whereby the melted plastics bonds the foil web to the substrate web and the 5 blown film is sealed to a surface of the foil web by the heat conducted from the plastics through the foil web; and it is said that this method reduces the outbreak of oxidative product to an extreme extent. The Patent pointed out that the plastics in the film blowing process can be pressed out of 10 the annular die at a temperature of 140°-180°C whereas in the corresponding slot-extrusion process the temperature is approximately 250°-325°C. It said that one of the very considerable advantages is that the blown film gives off appreciably less taste which is of particular importance in 15 the packaging of foodstuffs.

In one preferred embodiment in US-A-4,657,614 a carrier layer of paper or cardboard, coated beforehand with an outer polythene layer is passed over a cylinder and down into a nip between co-operating pressure and cooling cylinders. An Al 20 foil web is also guided in between the cylinders. Also introduced between the foil web and the carrier layer is a slot-extruded plastics layer. The warm plastics layer, not yet solidified, is then compressed, by the cylinders, between the carrier layer and one surface of the foil, a mechanical bond ensuing between the plastics and the carrier layer and 25 between the plastics and the foil, at the same time as the plastics cools down and becomes stabilised. A coextruded film manufactured beforehand and comprising two plastics layers, namely a plastics layer of the ethylene acrylic acid 30 (EAA) type and a plastics layer consisting of blown polythene is also introduced between the cylinders. Because those two plastics layers have been coextruded they have good adhesion to each other. The bulk of the heat content in the extruded plastics layer is given off to the foil since Al foil is a 35 much better heat-conductor than the paper material of the carrier layer. At the same time as the extruded plastics layer cools down and is stabilized the foil layer is thus heated and the heat is transferred to the EAA layer which has

a sealing temperature of approximately 93°C. Since the extruded plastics layer has to be heated to at least 300°C, it has a relatively large heat content which has to be dissipated. If the temperature and the thickness of the
5 extruded plastics layer are chosen correctly, sufficient heat for the achievement of a seal will be transferred to the EAA layer, which is raised thereby to a temperature exceeding 93°C and is made to melt therefore along its surface facing the foil layer and after cooling is bonded to the foil layer.

10 It seems that, in another preferred embodiment of US-A-4,657,614, the EAA layer is omitted and the blown film is melted by direct conduction of the heat from the Al foil but, because of the extremely short period of time between the blown film being subjected to the heat and its being cooled
15 by the cooling cylinder, the heating of the film does not give rise to any great amount of oxidative product.

20 The above solution has the disadvantage that it is limited to the production of laminates incorporating a layer of material, in practice metal foil, which is a good thermal conductor.

US-A-4,747,902 discloses that, in the extrusion laminating method, adhesive bonding mechanisms are classified into two kinds, i.e. mechanical adhesive bonding and chemical adhesive bonding. Mechanical adhesive bonding is relevant in
25 cases where porous substrate materials such as cloth and paper are used, in which the molten polymer, particularly PE, extruded at a high temperature infiltrates into fine pores among fibres and is then solidified by cooling, providing adhesive bonding between the PE and the substrate. Chemical adhesive bonding utilizes the chemical intermolecular force and it is employed for substrate materials having smooth surfaces such as regenerated cellulose film, Al foil and plastics films or those having no functional groups. In order
30 to obtain satisfactory bonding force in the chemical adhesive bonding, it is necessary that the substrate material be subjected to primer treatment, and it is often treated by corona discharge. It also mentions the preference that the PE used for extrusion coating be activated and that, as the method for this activation, it is a general practice that PE
35

is extruded at higher temperatures so as to increase oxygen-containing polar groups in molecules before it is brought into contact with a substrate material so as to provide sufficient adhesive strength.

5 The Patent adds that, with mechanical adhesive bonding, when the temperature of molten PE is high, its viscosity is low so improving the infiltration into the substrate material and thus the adhesive strength. Therefore, the lamination is done at temperatures as high as possible, provided that the
10 PE is not decomposed. Accordingly, low density polyethylene (LDPE) is heated to, at the lowest, 280° to 310°C in the conventional lamination process. In this process, it is necessary that the polyethylene is not decomposed and does not give out any offensive odour. In industrial practice,
15 however, partial decomposition is caused to occur, giving off an irritating smell from decomposed product, and much smoke is emitted during the processing.

We consider that this may be because the temperature readings given by the temperature detecting equipment of
20 conventional extruders do not necessarily represent the maximum temperatures actually attained in the extruders. In spite of their inaccuracy such readings are often used unquestioningly as accurate readings or as appropriate temperature settings in the present technical field.

25 In the solution proposed by US-A-4,747,902, the substrate is a sheet material and a layer of polyolefin (PO) laminated thereto. In a first method, a PO film to be laminated is used by being heated to a molten web and then applied to the PO of the substrate. In a second method,
30 extruded PO, as a molten web, is directly applied to the PO of the substrate material. In these methods, the temperature of the molten web is set as low as possible in order to avoid thermal deterioration of the polyolefin. That is, the temperature of the molten web is in the range between the melting point or softening point of the polymer to be laminated and a temperature higher than that temperature by 100°C. The laminate can be used for such things as fragrant books, bookmarks, pamphlets, tickets, name cards, postcards, telegram paper, fans, cores of rolled paper, labels, posters,

decorated building materials such as wall and ceiling materials, wrapping material, such as wrapping materials for lavatory tissue, greeting cards and letter paper, sealing paper for carton boxes of lavatory paper and casings of foodstuffs and flowers, refuse bags, waste bags, antifungal bags, antiseptic packaging materials for foodstuffs, mosquito repellent labels, insecticide sheets, wrapping sheets for growing fruits and rust-inhibitive packaging materials for steel pipes and machinery.

In an example, a substrate was prepared by conventional extrusion lamination at 300°C, in which a 20 micron thick layer of LDPE was applied to the surface of quality paper of 49g/m². After that, a 50 micron thick web of LDPE was extruded at 170°C and was laminated under pressure to the surface of the LDPE of the substrate to obtain the laminate.

The solution of US-A-4,747,902 has the disadvantages that it requires the provision of an additional layer of plastics to cover the plastics layer already coated onto the sheet material of the substrate and that the additional layer, unless undesirably thick, does not actually prevent permeation of the oxidation products.

According to one aspect of the present invention, there is provided a method of manufacturing a packaging laminate, comprising supplying a substrate providing a good barrier to transmission of oxygen, and applying to said substrate a thermoplastics, product-contact layer by extrusion through a die slot at an extrusion lamination station, adhesion between said product-contact layer and said substrate having been promoted, characterized in that the temperature of said product-contact layer is maintained below the breakpoint temperature of the thermoplastics material of said product-contact layer throughout said method.

According to a second aspect of the present invention, there is provided apparatus for use in manufacturing a packaging laminate, comprising an extruder including a die slot for producing a layer of thermoplastics material by extrusion, chilling means immediately downstream of said die slot for chilling said layer, means for supplying a substrate providing a good barrier to transmission of oxygen, roll

means for guiding said substrate to said layer, and adhesion-promoting means for promoting adhesion between said substrate and said layer, characterized in that said extruder is a low-temperature extruder.

Owing to these aspects of the present invention, and particularly whereby the thermoplastics material temperature is maintained below its breakpoint temperature throughout the method, the degree of oxidation of the material which can deleteriously affect the packaged product, especially produce off-flavour in packaged food, can be avoided. Furthermore, the fact that the substrate is a good barrier to oxygen minimizes transmittal of off-flavour-producing compounds from any other layers in the laminate to the outside of the barrier provided by the substrate. Moreover, the promotion of adhesion between the product-contact layer and the substrate provides for good adherence between the product-contact layer and the substrate in spite of extrusion of the product-contact layer below its breakpoint temperature.

The breakpoint temperature of a thermoplastics material is the temperature at which begins significant oxidation of the thermoplastics material in an air atmosphere.

The breakpoint temperature for a thermoplastics varies depending upon the particular composition of the thermoplastics. The breakpoint temperatures for a selection of thermoplastics each usable as the product-contact layer is given below:-

<u>Material (grade)</u>	<u>Melt flow</u>	<u>Breakpoint</u>
	<u>rate</u>	<u>temperature</u>
	<u>MFR</u>	<u>(°C)</u>
LDPE (high pressure autoclave)	4	250-280
LLDPE ("DOWLEX" 3010E)	5.5	260-280
Ionomer ("SURLYN" 1652)	5.5	260-280
EVA (16% Vinyl acetate)	3	220-240

The low-temperature extruder can be a substantially screwless rotary extruder with a gear pump; a planetary roller extruder with a gear pump; a twin-screw extruder; a screw extruder with a screw designed for low-temperature extrusion; or an extruder of the character conventionally used for cast film of the thermoplastics material.

The use of a low-temperature extruder has the advantage that the present system is readily applicable to a conventional extrusion-coating line, simply with replacement of a conventional, high-temperature, final extruder extruding the product-contact layer, by a low-temperature extruder performing the same function.

Adhesion between the product-contact layer and the substrate can be promoted by one or more of surface treatment (such as flame treatment, corona-discharge treatment, or plasma treatment) of the receiving surface of the substrate; applying an adhesive to that receiving surface, which application can be carried out either by a manufacturer of the substrate or in an extrusion-coating line producing the laminate; pre-heating of the substrate; "ALDYNE"® treating (employing electrodes to deposit a layer of glass on a substrate, particularly on an aluminium foil barrier layer); and co-extruding, in the low-temperature extruder, a low-temperature tie layer, for example "SURLYN"® or "PRIMACOR"®, in addition to the product-contact layer.

The substrate consists of a barrier layer constituting a good barrier to oxygen and thus to the passage towards the product-contact layer of oxidation or other compounds which would give an off-flavour to the product contact layer and/or the product. A material which is a good barrier to oxygen in the present context is a significantly better barrier to oxygen than is LDPE. To be a good barrier to oxygen, a 25-micron thick sheet of the material has an oxygen transmission rate (TR) lower than 1,000 millilitres/square metre/atmosphere pressure difference/day, and preferably has a TR lower than 100. Examples of such material are ethylene vinyl alcohol (EVOH), polyamide (PA), cellophane, greaseproof paper; and coatings of silicon oxide (SiO_x) (i.e. glass), metal (e.g. Al), and metal oxide (e.g. AlO_x). Thus the barrier layer may consist of one or more of metal (e.g. Al) foil; a polymeric barrier layer, e.g. EVOH or PA; a polymeric material coated by a deposition process (for example with a metal, metal oxide, or glass coating); greaseproof paper; and cellophane. The product-contact layer may be one or more polymers, especially one or more of PO, e.g. linear LDPE

(LLDPE), LDPE, very LDPE (VLDPE), high density polyethylene (HDPE) or polypropylene (PP); "METALLOCENE" POs; bi-modal POs; polyolefinic acid co-polymers (e.g. EAA); ionomers; ethylene vinyl acetate (EVA); blends of such polymers; and
5 filled such polymers.

Advantageously, the product-contact layer is of PO, preferably PE, most preferably LDPE with good organoleptic properties.

In order that the invention may be clearly understood
10 and readily carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:-

Figure 1 shows diagrammatically an extrusion-coating line manufacturing a packaging laminate, and

Figures 2 to 4 show diagrammatic cross-sections through
15 varieties of the laminate which can be produced by variations of the extrusion-coating line.

Referring to Figure 1, paperboard 1 is fed from a roll 3 to the nip between a pair of rollers 4 and 5 of a first extrusion lamination station of which the roller 5 is a chill roller. An alternate, ready roll 2 of paperboard is also shown. To the nip is supplied a molten film of PE from a die slot of a high-temperature extruder 7. The PE layer so supplied is to constitute the outside (with respect to a carton to be formed of the laminate) surface of the packaging
20 laminate. The web 2 so formed is forwarded to a second extrusion lamination station at which it enters the nip between a pair of rollers 8 and 9 of which the roller 9 is a chill roller. Also fed into the nip is a web 10 of an oxygen barrier substrate, in this example aluminium foil, fed from
25 a supply roll 11, whilst between the paperboard layer 1 and the aluminium foil web 10 is introduced a molten film 13 of a polymeric tie material from a die slot of a high-temperature extruder 12. The web 14 so formed then advances to a third and final extrusion lamination station at which it
30 passes between a pair of rollers 15 and 16, of which the roller 16 is a chill roller. Here, there is co-extruded, to between the aluminium foil layer 10 and the chill roller 16, a molten film 17 consisting of a polymeric tie layer 18 and a PE layer 19, which latter directly contacts the chill
35

roller 16. The molten film 17 is co-extruded from a low-temperature extruder 20 which is so positioned that its die slot 21 is at a horizontal level as close as practical to the horizontal level of the nip between the rollers 15 and 16, so as to minimise the potential for oxidation of the molten film 17, particularly of the product-contact PE layer 19, before it is cooled by the chill roller 16. The web 22 so formed is then wound onto a roll 23 for transport to, for example, a converting plant where the web is converted into blanks for forming liquid-packaging cartons in which the outside PE layer 6 is heat-and pressure-sealed to the inside, product-contact, PE layer 19. The manufacturing line illustrated in Figure 1 has the particular advantage that it can be formed by simply replacing the high-temperature, final extruder in a conventional extrusion-coating line with a low-temperature extruder 20. The low-temperature extruder 20 could be an "INSTAMELT"® rotary extrusion system available from Extrusion Systems, Inc., 1549 S. Fairground, Midland, Texas, United States of America, or a planetary roller extrusion system available from Entex Rust & Mitschke GmbH of Heinrichsstrasse 67, D-44805 Bochum, Germany.

An example of the packaging laminate produced on the line shown in Figure 1 is as follows:-

<u>Layer Reference No.</u>	<u>Layer Material</u>	<u>Preferred range of layer "thickness" (g/m²)</u>
6	LDPE	5-20
1	PAPERBOARD	140-450
13	LDPE	5-20
10	ALUMINIUM FOIL	15-25
30 18	"SURLYN"®	3-10
19	LDPE	10-50.

The LDPE supplied to the extruder 20 should not have been brought to a temperature at or above its breakpoint temperature prior to its entry into the extruder 20 and should not be raised to or beyond its breakpoint temperature at any point between entry into the extruder 20 and the chill roller 16. This is preferably also true of the tie layer 18.

An example of a packaging laminate produced on a variation of the line of Figure 1 is shown in Figure 2 and includes an oxygen barrier substrate 10 in the form of a film

27 of polyethylene terephthalate (PET) with a deposited coating 28 of Al or SiO_x. The substrate 10 is attached to the paperboard layer 1 and to the product-contact layer 19 by way of respective tie layers 25 and 29. The layer 29 may be co-extruded with the layer 19 and in those circumstances is such that its breakpoint temperature is above the co-extrusion temperature of the extruder 20. The coating 28 is to the inside of the PET film 27 to form a barrier against transmission of off-flavour-producing compounds from the PET film 27 towards the product.

An example of the packaging laminate of Figure 2 is as follows:-

<u>Layer Reference No.</u>	<u>Layer Material</u>	<u>Preferred range of layer "thickness" (g/m²)</u>
15	6 LDPE	5-20
	1 PAPERBOARD	140-450
	25 LDPE	5-20
	10 Al- or SiO _x -coated PET	8-20
	29 EMA	5-20
20	19 LDPE	10-50.

[EMA is ethylene meta-acrylic co-polymer].

Again, the LDPE supplied to the extruder 20 to constitute the LDPE layer 19 should not have been brought to a temperature at or above its breakpoint temperature prior to 25 its entry into the extruder 20 and should not be raised to or beyond its breakpoint temperature at any point between entry into the extruder 20 and the chill roller 16. This is preferably also true of the tie layer 29.

An example of a packaging laminate produced on another 30 variation of the line of Figure 1 is shown in Figure 3 and includes an oxygen barrier substrate 10 in the form of a layer 10 of EVOH extrusion-coated onto the inside of the to the paperboard layer 1. The layer 10 is attached to the product-contact layer 19 by way of a tie layer 32 of 35 anhydride-modified PO, preferably anhydride-modified LLDPE co-extruded with the layer 19 and having its breakpoint temperature above the co-extrusion temperature.

An example of the packaging laminate of Figure 3 is as

follows:-

<u>Layer Reference</u>	<u>Layer Material</u>	<u>Preferred range of layer "thickness" (g/m²)</u>
<u>No.</u>		
	6 LDPE	5-20
5	1 PAPERBOARD	140-450
	10 EVOH	3-25
	32 LLDPE	3-10
	19 LDPE	10-50.

The LDPE supplied to the extruder 20 to constitute the layer 19 should not have been brought to a temperature at or above its breakpoint temperature prior to its entry into the extruder 20 and should not be raised to or beyond its breakpoint temperature at any point between entry into the extruder 20 and the chill roller 16. This is preferably also true of the tie layer 32.

An example of a packaging laminate produced on a further variation of the line of Figure 1 is shown in Figure 4 and includes an oxygen barrier substrate 10 in the form of a film 35 of EVOH carrying tie layers 36 and 37 at the outside and the inside thereof. The substrate 10 is extrusion-laminated to the paperboard layer 1 by the LDPE 13 and the product-contact layer 19 is extrusion-coated on the layer 37. The layers 36 and 37 are of anhydride-modified PO, preferably anhydride-modified LLDPE.

An example of the packaging laminate of Figure 4 is as follows:-

<u>Layer Reference</u>	<u>Layer Material</u>	<u>Preferred range of layer "thickness" (g/m²)</u>
<u>No.</u>		
	6 LDPE	5-20
30	1 PAPERBOARD	140-450
	13 LDPE	5-20
	10 LDPE/EVOH/LDPE	8-20
	19 HDPE	10-50.

The HDPE supplied to the extruder 20 to constitute the LDPE layer 19 should not have been brought to a temperature at or above its breakpoint temperature prior to its entry into the extruder 20 and should not be raised to or beyond its breakpoint temperature at any point between entry into the extruder 20 and the chill roller 16.

CLAIMS

1. A method of manufacturing a packaging laminate, comprising supplying a substrate (10) providing a good barrier to transmission of oxygen, and applying to said substrate a thermoplastics, product-contact layer (19) by extrusion through a die slot (21) at an extrusion lamination station, adhesion between said product-contact layer (19) and said substrate (10) having been promoted, characterized in that the temperature of said product-contact layer (19) is maintained below the breakpoint temperature of the thermoplastics material of said product-contact layer (19) throughout said method.
5
2. A method according to claim 1, wherein the temperature of the thermoplastics of the product-contact layer (19) has been maintained below its breakpoint temperature prior to its supply to said extrusion lamination station.
10
3. A method according to claim 1 or 2, wherein said adhesion has been promoted by one or more of surface treatment of the receiving surface of the substrate (10); applying an adhesive to the receiving surface of the substrate (10); pre-heating of the substrate (10); employing electrodes to deposit a layer of glass on the substrate (10); and co-extruding, in a low-temperature extruder, a low-temperature tie layer (18) and the product-contact layer (19).
15
- 20
4. A method according to claim 1, 2 or 3, wherein said barrier layer (10) consists of one or more of metal foil, a polymeric oxygen barrier layer, a polymeric material coated by a deposition process, greaseproof paper, and cellophane.
25
5. A method according to any preceding claim, wherein said product-contact layer comprises one or more of a polyolefin, a polyolefinic acid co-polymer, an ionomer, and ethylene vinyl acetate.
30
6. Apparatus for use in manufacturing a packaging laminate, comprising an extruder (20) including a die slot (21) for producing a layer (19) of thermoplastics material by extrusion, chilling means (16) immediately downstream of said die slot (21) for chilling said layer (19), means (11) for supplying a substrate (10) providing a good barrier to transmission of oxygen, roll means (15) for guiding said
35

substrate (10) to said layer (19), and adhesion-promoting means (20,21) for promoting adhesion between said substrate (10) and said layer (19), characterized in that said extruder (20) is a low-temperature extruder (20).

5 7. Apparatus according to claim 6, wherein said low-
temperature extruder is one or more of a substantially
screwless rotary extruder with a gear pump; a planetary
roller extruder with a gear pump; a twin-screw extruder; a
screw extruder with a screw designed for low-temperature
10 extrusion; and an extruder of the character conventionally
used for cast film of said thermoplastics material.

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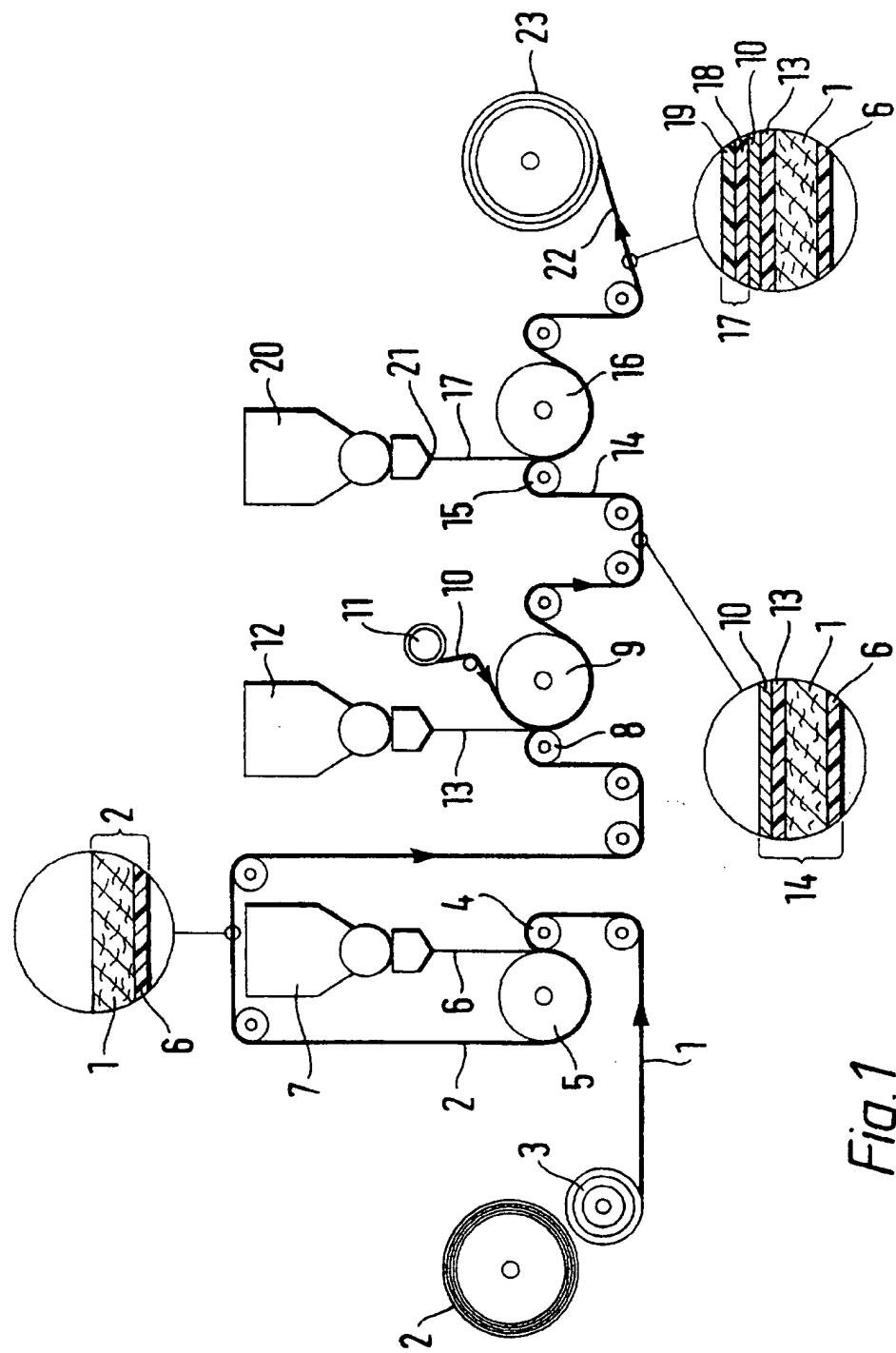


Fig. 1

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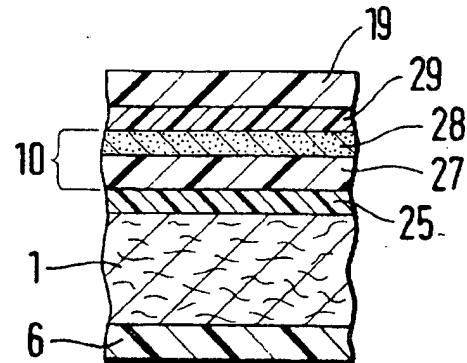


Fig. 2

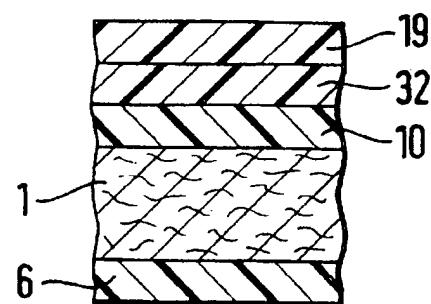


Fig. 3

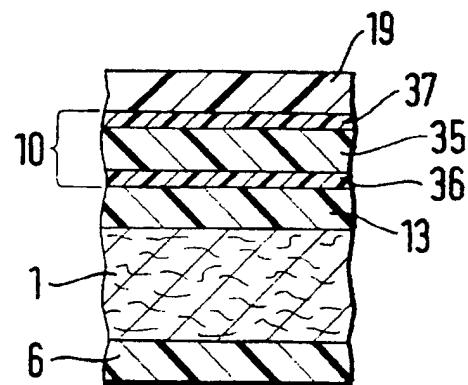


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/00263

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B32B31/30 B32B27/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B32B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 747 902 A (SAITO HACHIRO) 31 May 1988 cited in the application see abstract see column 2, line 60 - column 3, line 6; example ---	1-5
X	US 4 767 485 A (MICHIELS DIRK J M) 30 August 1988 see column 1, line 29 - line 45; claim 1 ---	1-5
X	US 4 020 215 A (MICHAEL LUBOMIR) 26 April 1977 see claim 14 ---	1-5
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *&* document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No PCT/IB 97/00263

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 388 (M-549), 25 December 1986 & JP 61 177224 A (SHOWA DENKO KK), 8 August 1986, see abstract ---	6,7
A	EP 0 520 767 A (WESTVACO CORP) 30 December 1992 see page 3, line 49 - line 51 ---	1-5
A	US 5 238 517 A (HEYES PETER J) 24 August 1993 see column 2, line 5 - line 21 ---	1-5
A	US 4 802 943 A (GIBBONS CHARLES E ET AL) 7 February 1989 see claims ---	1-5
A	EP 0 475 441 A (TOPPAN PRINTING CO LTD) 18 March 1992 see page 3, line 42 - line 56 -----	3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 97/00263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4747902 A	31-05-88	JP 1816236 C JP 5028171 B JP 62068728 A CA 1261736 A CA 1248417 A DE 3684851 A EP 0215480 A EP 0217275 A US 4808454 A	18-01-94 23-04-93 28-03-87 26-09-89 10-01-89 21-05-92 25-03-87 08-04-87 28-02-89
US 4767485 A	30-08-88	CA 1221281 A EP 0136874 A	05-05-87 10-04-85
US 4020215 A	26-04-77	NONE	
EP 0520767 A	30-12-92	CA 2070349 A JP 2537000 B JP 5229070 A	27-12-92 25-09-96 07-09-93
US 5238517 A	24-08-93	AU 606479 B AU 2555888 A BG 50043 A CA 1337260 A CN 1032763 A DE 3867415 A EP 0312309 A FI 96397 B WO 8903301 A GB 2211140 A,B HR 930113 A HR 930117 A JP 2501642 T KR 9605300 B PL 163969 B RU 2069154 C	07-02-91 02-05-89 15-04-92 10-10-95 10-05-89 13-02-92 19-04-89 15-03-96 20-04-89 28-06-89 31-12-95 31-12-95 07-06-90 23-04-96 30-06-94 20-11-96
US 4802943 A	07-02-89	US 4789575 A AT 118734 T AU 611154 B AU 1672988 A	06-12-88 15-03-95 06-06-91 01-12-88

INTERNATIONAL SEARCH REPORT

Information on patent family members

In. International Application No

PCT/IB 97/00263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4802943 A		CA 1326645 A DE 3853099 D DE 3853099 T EP 0293098 A ES 2072861 T FI 89567 B JP 63312143 A KR 9512792 B NO 177562 B US RE33376 E ZA 8802901 A	01-02-94 30-03-95 14-06-95 30-11-88 01-08-95 15-07-93 20-12-88 21-10-95 03-07-95 09-10-90 27-10-88
EP 0475441 A	18-03-92	AU 645128 B AU 8386491 A CA 2051219 A JP 5008318 A US 5314561 A	06-01-94 19-03-92 15-03-92 19-01-93 24-05-94